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(54) Title: INK-JET INK COMPOSITION

(57) Abstract: A water-based ink-jet ink composition comprises: (a) an emulsion of a cross-linkable oligomer or polymer comprising at least one reactive carbonyl group capable of reacting with a cross-linking agent (b); (b) a cross-linking agent which cross-links the oligomer or polymer in (a) upon drying of the composition; and (c) a resolubilising polymer. This composition has a viscosity at 25 °C of no more than 50 centipoise, preferably no more than 30 centipoise, more preferably no more than 15 centipoise, and especially no more than 5 centipoise.

## INK-JET INK COMPOSITION

The present invention relates to a composition for an ink-jet ink.

Ink-jet printing has been used both for home/office as well as industrial and commercial applications such as coding, cable marking, wide-format poster and vinyl sheet printing, and business forms. For many of these applications organic solvent-based systems have been used. However, on the one hand environmental and health and safety concerns make it desirable to minimise the organic solvent content. On the other hand, systems which are substantially aqueous based present other problems. For example, the print is not very durable or water-fast, particularly on non-absorbent surfaces such as plastics substrates.

The organic solvent-based systems can still have durability problems. Thus, for industrial printing onto e.g. plastics substrates, it has been proposed in WO-A-97/31071 to formulate solvent-based ink-jet inks which are curable after printing, by application of ultraviolet (UV) light, in order to harden the print. This approach, using a variety of UV-curing systems, has also been described in EP-A-465 039, EP-A-540 203, US-A-4 303 924 and US-A-5 270 368. Whilst this is one solution to the problem of lack of print durability, use of organic solvents is preferably minimised or avoided for the reasons mentioned above. Moreover, the use of a UV source is undesirable for reasons of cost and complexity.

Therefore, there remains a need for a water-based ink-jet ink which overcomes the problems of lack of print durability and poor water-fastness. In conventional (non-ink-jet) printing inks and certain other surface coatings applications, another technique which has been used to harden the print, instead of UV curing, is use of air-drying cross-linker systems, that is to say, compositions containing polymers and cross-linking agents

in which cross-linking only occurs upon drying i.e. on evaporation of the water and any other solvent present.

US-A-3 345 336 discloses the manufacture of homopolymers and copolymers of unsaturated keto compounds which are cross-linked by polyfunctional carboxylic acid hydrazides. Such materials have long been used for surface coatings such as wood stains.

Another such air-drying cross-linking system is disclosed in WO 95/29944 which comprises an aqueous emulsion of an emulsion polymerised acid functional oligomer having a  $T_g$  below 50 °C having cross-linker functional groups, the resulting emulsified product being an olefinic hydrophobic polymer having a  $T_g$  of at least 25 °C. Typical polymers are copolymers of butyl acrylate and methyl methacrylate, the cross-linker functional groups being diacetone acrylamide groups. The cross-linking agent is, typically, adipic acid dihydrazide. Preferably, the compositions also contain a non-acid functional, non-cross-linking comonomer. Although mainly described for use in wood stains, these compositions are also disclosed for use in a wide range of other coating applications, including inks. However, use in low viscosity ink-jet formulations is neither disclosed nor hinted at.

JP-A-7026196 discloses surface treatment compositions for use as printing inks, paints and sealants, for plastics, metal, paper or glass substrates. These contain an emulsion of a resin having an aldo or keto group and a carboxyl group, obtained by emulsion polymerisation of an ethylenically unsaturated compound in the presence of a water-soluble resin that is obtained by neutralising a resin containing aldo or keto groups and carboxy groups using ammonia or an organic amine. The composition also contains a cross-linking agent having at least two hydrazine residues.

US-A-5 567 747 describes a different drying mechanism which employs an oxidatively drying system of epoxy ester, cyclodextrin and a catalytic drier in the formulation of a flexographic printing ink. A problem is that, once dry, such emulsions have very poor

resolubility i.e. they do not easily re-dissolve in the original ink. In ink jet printers which have very small diameter nozzles, this can lead to clogging of the nozzles with dried ink over a period of time. However, it is well known to those skilled in the art that the resolubility of aqueous emulsions can often be improved to an acceptable level by the addition of a water-soluble polymer, whilst still maintaining the water resistance of the final dried print.

Air-drying self cross-linking acrylic silicone copolymers have been proposed for use in water-based ink-jet ink formulations in JP-A-10-316908 and JP-A-10-140058. These references respectively relate to systems incorporating a water-solubilising polymer and systems with an oil-emulsion as a resolubilising agent.

Thus, in a first aspect, the present invention now provides a water-based ink-jet ink composition comprising:-

- (a) an emulsion of a cross-linkable oligomer or polymer comprising at least one reactive group capable of reacting with a cross-linking agent;
- (b) a cross-linking agent which cross-links the oligomer or polymer in
  - (a) upon drying of the composition; and
  - (c) a resolubilising polymer,

wherein the composition has a viscosity at 25 °C of no more than 50 centipoise, preferably no more than 30 centipoise, more preferably no more than 15 centipoise, and especially preferably no more than 5 centipoise.

A second aspect of the present invention provides a method of printing on a substrate, comprising applying to said substrate an ink-jet ink comprising a composition according to the first aspect of the invention, and allowing or causing said ink to dry upon the substrate.

The compositions of the present invention provide one or more advantages over the air-drying systems of JP-A-10-316908 and JP-A-10-140058 by virtue of incorporating a distinct cross-linking agent (b). These advantages, depending on the precise nature of the formulation, are selected from one or more of better water-fastness, better adhesion, adhesion to a wider range of substrates, better print durability and better re-solubilising behaviour.

Until now, nobody has realised that these air-drying cross-linker systems could find application in aqueous-based ink-jet inks and solve the aforementioned durability and water-fastness problems. Ink-jet inks necessarily have a room temperature viscosity far below that of normal printing inks. In particular, systems based on acrylic emulsions are particularly advantageous. Ink-jet inks have a very low room temperature viscosity and it can be difficult to make ink formulations with sufficient levels of resin to achieve satisfactory dry film properties. However, the emulsion form of these air-drying cross-linker systems gives them inherently low viscosity at high solids levels making them ideally suited to ink-jet ink formulation. In addition, ink-jet inks according to the invention are very storage stable. This stability is especially enhanced when they are formulated to be alkaline, e.g. having a pH of from 7.5 to 10.0, more preferably from 8.0 to 9.5.

Component (a) is a polymer emulsion, specifically an emulsion of an oligomer or polymer having reactive groups capable of being cross-linked by the cross-linking agent (b) when the composition dries. Preferably, it is an acrylic-type polymer emulsion. Preferably, the reactive group(s) comprise reactive carbonyl groups (e.g. having keto or aldehyde functionality) but, in principle, they may be chosen from a wide range of groups, such as epoxy (preferably glycidyl) and hydroxyalkyl (preferably C<sub>1</sub> to C<sub>12</sub> e.g. hydroxyethyl) methacrylates and acrylates. Suitable keto and aldehyde functional monomers include acrolein, methacrolein, vinyl methyl ketone, the acetoacetoxy esters of hydroxyalkyl (preferably C<sub>1</sub> to C<sub>12</sub>) acrylate, as well as keto-containing amides, for example diacetone acrylamide.

Normally, such materials are commercially supplied as aqueous emulsions of the polymer with the cross-linking agent (b) already dissolved in the aqueous phase. The component (a) remains in emulsified form when incorporated in the ink composition.

Other monomer units incorporated in the oligomer or polymer of emulsion (a) (i.e. in addition to those containing the reactive cross-linkable groups) may be chosen from a wide range of possibilities to import other desirable properties, such as to provide stability and film forming properties, for example one or more selected from carboxyl functional monomers (e.g. acrylic acid, methacrylic acid, itaconic acid, crotonic acid), acrylate esters (e.g. ethyl acrylate, butyl acrylate, ethylhexyl acrylate.), methacrylate esters (e.g. methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, isobornyl methacrylate), styrenes and substituted styrenes such as alpha-methyl styrene. The use of these monomers is cited in the aforementioned patent literature.

The oligomer or polymer in emulsion (a), preferably has a weight average molecular weight of from 500 to 5,000,000, more preferably from 3,000 to 3,000,000, these molecular weights being those determined using the method of gel permeation chromatography, using an appropriate known polymer as standard.

For carbonyl-containing (e.g. keto or aldehyde) reactive groups in component (a), the cross-linking agent (b) may comprise a di- or polyamine and/or di- or polyhydrazide, such as oxalic acid dihydrazide, phthalic acid dihydrazide, terephthalic acid dihydrazide, isophorone diamine or 4,7-dioxadecene - 1,10-diamine, or selected from derivatives of dibasic acids (e.g. adipic dihydrazide, succinic dihydrazide, phthalic acid dihydrazide) dialkylamine derivatives of polyalkyl glycols, and alkyl di- or triamines such as isophorone diamine. When the reactive groups of component (a) are hydroxyl groups, suitable cross-linking agents (b) are polyisocyanates, melamine and glycoluril.

There exist many commercial examples of such air-drying cross-linker systems containing components (a) and (b) together, for example Acronal D6079 and Acronal A603 (ex BASF), Esicryl 1000XL (ex Cook Composites & Polymers (CCP)), Neocryl

XK12 and Neocryl BA-820-B (ex Zeneca Resins), Setalin XD1160 and Setalin XD1134 (ex Akzo Nobel Resins).

Preferably, the amount of the oligomer or polymer material *per se* from emulsion (a) is present at from 5% to 40%, more preferably from 10% to 35%, by weight of the total ink composition.

Whether or not it is introduced to the ink in solution with component (a), preferably the amount of the cross-linking agent (b) is determined by the ratio of reactive equivalents, which can typically be from 4:1 to 1:4 or, more preferably, from 2:1 to 1:2.

Another essential component of compositions according to the present invention is the resolubilising polymer (c). The polymer (c) is included in the composition for the purpose of ensuring resolubilisation of any partially dried ink, e.g. around the ink jet print head nozzle, in order to keep the apparatus clean and the ink free-flowing. It is preferably included in the ink in an amount of from 0.5% to 10%, more preferably from 1% to 8%, by weight of the total composition.

The resolubilising polymer is preferably a water-soluble polymer, more preferably a polymer containing carboxylic acid groups which is soluble only when these groups are neutralised with an alkali such as ammonia or a volatile amine like dimethylethanolamine or monoethanolamine. This latter approach has the advantage that the resolubilising polymer is then only soluble in the presence of both water and an alkali, which produces less of a reduction in the water-fastness of the dried ink film than would a truly water-soluble polymer.

Examples of truly water-soluble resolubilising polymers include sulphopolyesters, polyvinyl pyrrolidones and polyvinyl alcohols. There are also many examples of polymers which may be rendered water soluble by virtue of their carboxylic acid functionality e.g. maleic resins, fumaric resins, styrenated maleic anhydride resins, polyamide resins, acrylic copolymer resins and acrylic emulsions. Any of the foregoing

polymers may be used alone or in combination. Whilst the selection of the resolubilising resin is limited only by the compatibility with the self-cross-linking emulsion, a particularly useful choice is from the very wide range of commercially available acrylic copolymer resins and emulsions. Pigment may easily be ground into these acrylic polymers to produce stable dispersions with high colour strength and gloss. These materials typically have an acid value of from 100 to 300, preferably from 150 to 250, mg/mole KOH. The resins have a weight average molecular weight between 1,500 and 20,000, preferably between 5,000 and 15,000. Examples include Joncryl 678 and Joncryl 683 (ex S. C. Johnson), Morez 100 and Morez 300 (ex Morton). The emulsions have a weight average molecular weight between 25,000 and 55,000, preferably between 35,000 and 45,000. Examples include Joncryl 142 (ex S. C. Johnson), Neocryl BT-26 (ex Zeneca) and Lucidene 196 (ex Morton).

Compositions according to the present invention preferably contain from 60% to 85%, more preferably from 70% to 80%, by weight of water.

The compositions of the present invention necessarily have a low viscosity of 25 °C, i.e. no more than 50 centipoise (cP), preferably no more than 30 centipoise, and more preferably no more than 15 centipoise, for drop on demand (DOD) printing and no more than 5 cP for continuous printing. These viscosities are expressed as those measured on a Brookfield DV-II viscometer and a UL adapter spindle 0, at a shear rate of 60 s<sup>-1</sup>.

Known compositions having air-drying cross-linking systems which have been used for non-ink-jet applications, typically contain other materials and/or are formulated differently, so that they have a higher viscosity than an ink-jet ink, which must have a very low viscosity. The ink-jet inks according to the present invention can easily be formulated by the person skilled in the art to have the required low viscosity. The basic air-drying emulsion itself will normally have a relatively low viscosity and the amount of the water and/or choice of, and amounts of, co-solvent and/or the total amount of solids, can easily be adjusted to achieve a particular desired viscosity.

As used herein, the term "ink-jet ink composition" encompasses both compositions which already contain colourant and those without colourant, being a base to which an ink manufacturer can add one or more colourants of choice. However, when supplied commercially for immediate use, ink-jet ink compositions according to the present invention will normally already contain colourant. Broadly speaking, colourants may be considered as falling into two classes, namely dyes, which are substantially soluble in the ink composition, and pigments, which are dispersed in the ink composition in the form of fine particles, if necessary with the aid of a suitable dispersant. The term "colourant" also includes materials which endow a non-visible optical property (e.g. fluorescence) to the ink.

Where dyes are employed, these may be selected from a wide range of classes, so long as they are soluble in the ink vehicle. Suitable types of dye include acid dyes, basic dyes, reactive dyes and those solvent dyes which are water-soluble or water-dispersible. A wide range of appropriate commercially available types will be well known to those skilled in the art.

However, the object of this invention is to produce prints with a high degree of resistance properties. In most cases, dyes have relatively poor resistance properties, for example to water and to light. A pigment will therefore normally be chosen as the colourant. Pigments may be selected from a wide range of classes including azo pigments (monoarylide, diarylide, naphthol, benzimidazolone, metal salt reds), phthalocyanines, quinacridones and dioxazines, for example Pigment Red 57:1, Pigment Red 52:2, Pigment Red 48:2, Pigment Blue 15:3, Pigment Green 7, Pigment Yellow 83, Pigment Yellow 13, Pigment White 6, Pigment Black 7. A non-exhaustive list of examples of such pigments include the following from the Irgalite range (ex CIBA): Rubine L4, Bordeaux CM, Red 2BP, Blue LG, Green GLN, Yellow B3R and yellow LBG; as well as Tioxide RHD6 (ex Tioxide) and Special Black 250 (ex Degussa).

When present, the total amount of colourant in the composition is typically from 1% to 15%, preferably from 2% to 10%, by weight of the total composition.

Ink-jet ink compositions according to the present invention may contain other optional components such as organic solvents, surfactants, slip and scratch resistance additives, anti-foams and biocide.

One or more organic solvents such as alcohols and polyols (e.g. ethyl alcohol and isopropyl alcohol), glycols (e.g. propylene glycol, diethylene glycol), glycol ethers (e.g. methoxypropanol) and glycol ether acetates (e.g. methoxylpropyl acetate) may be included to adjust drying speed and improve wetting on low surface energy plastic surfaces. Generally speaking, if present, the total amount of organic solvent is from 1% to 10% by weight of the total composition.

Water has a high surface tension and surfactants may therefore be included in the formulation to reduce the surface tension of the composition to aid in the wetting of low surface energy, non-absorbent surfaces, especially plastics surfaces. Useful surfactant classes include anionic surfactants (e.g. sulphosuccinates), non-ionic surfactants (e.g. acetylenic diols, polyethylene/polypropylene oxides) and fluorosurfactants. Generally speaking, if present, the total amount of surfactant is from 0.1 to 5% by weight of the total composition.

The surface slip, scratch and rub resistance of the dried ink film can be improved by the addition of low levels of surface active materials such as silicones and waxes. Generally speaking, if present, the total amount of these additives together will be between 0.1 and 5% by weight of the total composition.

The formation of foam can be a problem in water-based ink-jet inks, particularly where the ink is agitated during use such as in continuous printing. This can be controlled by the use of anti-foams and defoamers, either silicone-based or silicone-free. A wide variety of chemistries and products are commercially available. Generally speaking, if present, the total amount of anti-foam is from 0.1% to 1.0% by weight of the total composition.

The aqueous environment provides an ideal breeding ground for microbes. A biocide is therefore included in the composition to extend the shelf life e.g. a 1,2-benzisothiazolyn-3-one type biocide such as Proxel CF (ex Zeneca), at a level of less than 1%, normally no more than 0.1%, by weight of the total composition.

The invention will now be further explained by reference to the following non-limiting examples.

Example 1

|   |         |
|---|---------|
| Self cross-linking emulsion, Acronal A603 (ex BASF) <sup>1</sup>  | 21.50%  |
| 25% Solids solution in de-ionised water of alkali soluble resin, Joncryl 678<br>(ex SCJohnson Polymer) <sup>2</sup> (neutralised to a pH of 9.0-9.5<br>with dimethylethanolamine) | 12.90%  |
| Black pigment (Colour Index PB17), Elftex 435 (ex Cabot)  | 7.40%   |
| De-ionised water  | 57.53%  |
| Acetylenic diol surfactant, Surfynol 104 (ex Air Products)  | 0.50%   |
| Silicone antifoam, Agitan E256 (ex Munzing Chemie GmbH)   | 0.15%   |
| Biocide, Proxel CF (ex Zeneca)  | 0.02%   |
| <hr/>   |         |
|   | 100.00% |

The black pigment is pre-dispersed into the resin solution in a bead mill.

Properties:

- Viscosity = 3.0 cP @ 25°C
- Conductivity = 4800 µS/cm
- Surface tension = 37.5 dynes/cm
- pH = 8.1
- Adhesion to polythene (corona discharge treated to a surface energy of 38 dynes/cm)  
when dried with warm, fast-moving air = excellent (no ink removal using adhesive  
tape)
- Wet rub resistance on polythene (corona treated as above). Slight ink removal after  
50 hand rubs with a damp cotton bud.
- Suitable for continuous ink-jet printing

Example 2

|  |         |
|--|---------|
| Self cross-linking emulsion, Esicryl 1000XL (ex Cook Composites) <sup>1</sup>  | 29.10%  |
| 25% Solids solution in de-ionised water of alkali soluble resin,<br>Joncryl 683 (ex SCJohnson Polymer) <sup>2</sup> (neutralised to a pH of 9.0-9.5<br>with ammonia) | 12.20%  |
| Black pigment (Colour Index PB17), Elftex 435 (ex Cabot)   | 2.70%   |
| De-ionised water   | 47.44%  |
| Solvent, methoxypropyl acetate   | 7.30%   |
| Acetylenic diol surfactant, Surfynol 420 (ex Air Products)   | 1.00%   |
| Silicone antifoam, Tegofoamex 1488 (ex Tego Chemie)  | 0.25%   |
| Biocide, Proxel CF (ex Zeneca)   | 0.01%   |
| <hr/>  |         |
|  | 100.00% |

The black pigment is pre-dispersed into the resin solution in a bead mill.

Properties:

- Viscosity = 3.6 cP @ 25°C
- Conductivity = 4800 µS/cm
- Surface tension = 37.5 dynes/cm
- pH = 8.5
- Adhesion to polythene (corona discharge treated to a surface energy of 38 dynes/cm) when dried with warm, fast-moving air = excellent (no ink removal using adhesive tape).
- Wet rub resistance on polythene (corona treated as above). No ink removal after 50 hand rubs with a damp cotton bud.
- Suitable for continuous ink-jet printing.

Example 3

|  |         |
|--|---------|
| Self-crosslinking emulsion, Setalin XD1134 (ex Akzo Polymers) <sup>1</sup>                                     | 40.00%  |
| 25% solids solution in de-ionised water of alkali soluble resin,   |         |
| Morez 100 (ex Morton International) <sup>2</sup> (neutralised to a pH of 9.0-9.5<br>with dimethylethanolamine) | 4.20%   |
| Black water soluble dye solution, Bascript Black SP Liquid (ex BASF)   | 10.00%  |
| De-ionised water   | 45.68%  |
| Silicone antifoam, Tegofoamex 1488 (ex Tego Chemie)  | 0.10%   |
| Biocide, Proxel CF (ex Zeneca)   | 0.02%   |
|  | -----   |
|  | 100.00% |

## Properties:

- Viscosity = 2.3 cP @ 25°C
- Conductivity = 6180 µS/cm
- Surface tension = 43 dynes/cm
- pH = 8.4
- Adhesion to polythene (corona discharge treated to a surface energy of 38 dynes/cm) when dried with warm, fast-moving air = excellent (no ink removal using adhesive tape). The ink reticulates on the polythene surface.
- Wet rub resistance on polythene (corona treated as above). Significant ink removal after 10 hand rubs with a damp cotton bud.
- Suitable for continuous ink-jet printing.

Example 4

|  |         |
|--|---------|
| Self cross-linking emulsion, Esicryl 1000 XL,<br>(ex Cook Composites & Polymers) <sup>1</sup>  | 51.80%  |
| 25% Solids solution in de-ionised water of alkali soluble resin,<br>Joncryl 683 (ex SCJohnson Polymer) <sup>2</sup> (neutralised to a pH of 9.0-9.5<br>with ammonia) | 13.00%  |
| Black pigment (Colour Index PB17), Printex 30 (ex Degussa)   | 3.00%   |
| De-ionised water   | 27.18%  |
| Solvent, diethylene glycol   | 5.00%   |
| Biocide, Proxel CF (ex Zeneca)   | 0.02%   |
|  | -----   |
|  | 100.00% |

The black pigment is pre-dispersed into the resin solution in a bead mill

Properties:

- Viscosity = 11.5 cP @ 25°C
- Surface tension = 37.5 dynes/cm
- pH = 8.1
- Adhesion to polythene (corona discharge treated to a surface energy of 38 dynes/cm) when dried with warm, fast-moving air = excellent (no ink removal using adhesive tape).
- Wet rub resistance on polythene (corona treated as above). No ink removal after 50 hand rubs with a damp cotton bud.
- Suitable for Drop On Demand ink-jet printing.

Example 5

|  |         |
|--|---------|
| Self cross-linking emulsion, Neocryl BA-820-B (ex Zeneca Resins) <sup>1</sup>  | 21.20%  |
| 20% Solids solution in de-ionised water of alkali soluble emulsion, Neocryl BT-26 <sup>2</sup> (ex Zeneca Resins) (neutralised to a pH of 9.0-9.5 with monoethanolamine) | 12.90%  |
| Flexiverse Blue 15 : 3 aqueous dispersion (ex Sun Chemical)  | 8.50%   |
| De-ionised water   | 56.78%  |
| Sulphosuccinate surfactant, Aerosol OT (ex Cytec Industries)   | 0.50%   |
| Silicone antifoam Tegofoamex 1488 (ex Tego Chemie)   | 0.10%   |
| Biocide, Proxel CF (ex Zeneca)   | 0.02%   |
|  | -----   |
|  | 100.00% |

## Properties:

- Viscosity = 3.5 cP @ 25°C
- Conductivity = 4500 µS/cm
- Surface tension = 38.5 dynes/cm
- pH = 8.5
- Adhesion to polythene (corona discharge treated to a surface energy of 38 dynes/cm) when dried with warm, fast-moving air = excellent (no ink removal using adhesive tape).
- Wet rub resistance on polythene (corona treated as above). Slight ink removal after 50 rubs with a damp cotton bud.
- Suitable for continuous ink-jet printing.

Raw Materials

<sup>1</sup> An emulsion of an acrylic co-polymer including reactive keto-functionality, and a polyamine or polyhydrazide cross-linker.

<sup>2</sup> An acrylic co-polymer including carboxylic acid functionality.

**CLAIMS:**

1. A water-based ink-jet ink composition comprising:
  - (a) an emulsion of a cross-linkable oligomer or polymer comprising at least one reactive group capable of reacting with a cross-linking agent (b);
  - (b) a cross-linking agent which cross-links the oligomer or polymer in (a) upon drying of the composition; and
  - (c) a resolubilising polymer,

wherein the composition has a viscosity at 25 °C of no more than 50 centipoise, preferably no more than 30 centipoise, more preferably no more than 15 centipoise, and especially preferably no more than 5 centipoise.

2. A composition according to claim 1, wherein the oligomer or polymer in emulsion (a) comprises at least one reactive carbonyl group.
3. A composition according to either preceding claim, wherein the cross-linking agent (b) comprises a di- or poly-amine and/or a di- or poly-hydrazide.
4. A composition according to any preceding claim, wherein the resolubilising polymer is selected from carboxyl-containing polymers which are only water-soluble when neutralised with an alkali.
5. A composition according any preceding claim, wherein the amount of the oligomer or polymer (a) is from 5% to 40%, preferably from 10% to 35%, by weight of the total composition.
6. A composition according to any preceding claim, wherein the amount of the cross-linking agent (b) is such that the number ratio of the reactive equivalents in (b) to the reactive equivalents in (a) is from 4 : 1 to 1 : 4, preferably from 2 : 1 to 1 : 2.

7. A composition according to any preceding claim, wherein the amount of the resolubilising polymer (c) is from 0.5% to 10%, preferably from 1% to 8%, by weight of the total composition.
8. A composition according to any preceding claim, comprising the water in an amount from 60% to 85%, preferably from 70% to 80%, by weight of the total composition.
9. A composition according to any preceding claim, comprising colourant in an amount of from 1% to 15%, preferably from 2% to 10%, by weight of the total composition.
10. A composition according to any preceding claim, comprising surfactant in an amount of from 0.1% to 5%, by weight of the total composition.
11. A composition according to any preceding claim, comprising organic solvent in an amount of from 1% to 10%, by weight of the total composition.
12. A method of printing on a substrate, comprising applying to the substrate an ink-jet ink comprising a composition according to any of claims 1 to 11, and allowing or causing the ink to dry upon the substrate.

# INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/GB 00/04277

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|----------|--|-----------------------|
| A        | EP 0 617 097 A (CANON KK)<br>28 September 1994 (1994-09-28)<br>page 5, line 5 -page 7, line 27<br>page 8, line 12-16<br>---  | 1-5, 8, 9,<br>11, 12  |
| A        | EP 0 767 225 A (SEIKO EPSON CORP)<br>9 April 1997 (1997-04-09)<br>page 3, line 45-53<br>page 4, line 8-27<br>page 4, line 53 -page 5, line 9<br>page 6, line 7-39<br>--- | 1, 4, 6,<br>10-12     |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

### \* Special categories of cited documents :

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Date of the actual completion of the international search

29 January 2001

Date of mailing of the international search report

13/02/2001

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